



A low carbon route to ethylene: Ethane oxidative dehydrogenation with CO₂ on embryonic zeolite supported Mo-carbide catalyst

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ABSTRACT

The study reports a novel catalyst based on supported molybdenum-carbide (Mo₂C) phase for oxidative dehydrogenation of ethane with CO₂ (ODH-CO₂). The optimal result is obtained with MoS₂-precursor as the intermediate supported on a non-acidic embryonic zeolite, which is transformed in situ to Mo₂C (Mo₂C@EZ). The ultimate catalyst and its intermediates are characterized. 66% conversion of ethane, 58% of ethylene yield, and 56% conversion of CO₂ to CO with the in situ co-produced hydrogen obtained from ethane to ethylene transformation are the achievements of utilizing Mo₂C@EZ. The performed techno-economic study on Mo₂C@EZ results in a potentially CO₂ negative route for ethylene production with 109% of CO₂ reduction per ton of produced ethylene in comparison with a conventional ethane cracker. The process is expected to be cheaper in capital expenditure (CAPEX) and operating expenses (OPEX) thanks to a simpler product slate, lower energy demand, and no requirement for steam dilution.

1. Introduction

Ethylene is the largest-volume petrochemical building block, produced primarily by steam cracking of oil fractions [1]. In 2020, the worldwide ethylene production capacity was 201 million tons, with an expected increase to 263 million tons in 2030 [2,3]. Ethylene is used to produce a wide spectrum of products like plastics, fibers, and other chemicals in the packaging, transportation, and construction industries. Polyethylene is the single-largest outlet, accounting for about 60% of global ethylene consumption in 2020. Other major applications include the production of ethylene oxide, ethylene dichloride, and ethylbenzene.

Steam cracking of oil fractions is the major process currently used to produce ethylene; a smaller contribution comes from refinery processes such as fluid catalytic crackers and cokers. It is a mature and well-established technology, which operation is considered near-optimal considering constant incremental improvements of the technology over 80⁺ years [4,5], leading to a thermal efficiency of close to 95% [6]. However, cracking is a very endothermic reaction taking place at high temperatures. As a result, ethylene production via steam cracking consumes about 30% of the energy used in the chemical industry. In

particular, as ethylene production by steam cracking consumes roughly between 17 and 25 GT/ton of ethylene while releasing about 1.2 tons of CO₂ per ton of olefin produced [5]; it is with about 260 million tons of CO₂ emissions worldwide per year [6], one of the largest contributors to greenhouse gas emissions in the manufacturing sector. Alternative routes and feedstocks need to be explored and developed to foster sustainable development of olefins production. In the last decade, the ongoing shift to lighter hydrocarbons as steam cracking feedstock has prompted research and development of alternative on-purpose production routes to ethylene.

One of the options for sustainable ethylene production is in the utilization of bio feedstock: either bioethanol or bio hydrocarbon fractions [7–9]. Bioethanol dehydration shows advantages in energy consumption and in capital investments relative to conventional steam cracking due to simpler product slate and lower reaction temperature. Until the mid-1940 s, a significant portion of the ethylene produced industrially was produced from bioethanol. Afterward, steam cracking of hydrocarbons, because of their superior economies of scale and lower feedstock costs, became the main source of ethylene. Currently, with the significantly increased cost of natural gas and crude oil together with the need to reduce the carbon intensity of the petrochemical industry, the

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downstream industry is renewed interest in ethylene-from-ethanol plants [10,11]. So, this route will certainly regain importance but will not fulfill the total demand for ethylene due to the competition for the feedstock with biofuel production. The availability of bio-naphtha and bio-propane as a feedstock for olefins production is still limited [8]. The direct conversion of the cellulosic biomass or bio-oil remains an attractive route but mainly provides aromatic fractions [12–14].

So, a reduction of the carbon intensity of ethylene production routes remains a very important task for the petrochemical industry. The oxidative dehydrogenation of ethane (ODH) shows good prospects to reduce greenhouse gases emissions in comparison to a conventional ethane cracker due to a number of advantages, including lower energy consumption, simpler production slate, and potential elimination of the equilibrium limitations [15,16]. One of the main limitations remains the development of an efficient and stable high-temperature catalyst. Already in the early 80's, Phillips Petroleum proposed the first industrial Li-SnCl₂-MgO catalyst for oxidative dehydrogenation of ethane with oxygen [17]. This process did not require acetylene hydrogenation and had the potential to reduce energy consumption in an ethylene plant, allowing operations at 700 °C instead of 850 °C, and providing a higher ultimate yield of 90.5% ethylene [17] compared to the thermal process. However, as CO₂ was an important by-product, the economics were not better than state-of-the-art steam crackers. Recently, the topic regain attention the two semi-commercial oxidative dehydrogenation (ODH) of ethane processes were proposed [18–20]. Oxygen as an oxidant could be used in gaseous form or from catalysts' metal oxides lattice. One such promising on-purpose Oxidative Dehydrogenation of Ethane (ODH-E) technology is proposed by the Linde/Clariant partnership; a high selectivity to valuable products (ethylene and acetic acid) compared to steam cracking combined with a significant reduction potential of the CO₂ footprint is promised. Moreover, the reaction takes place under mild conditions, for instance, at atmospheric pressure and a maximum temperature of 400 °C [21]. However, as oxygen is applied as an oxidant, CO₂ is still present in products.

Another ODH option is based on chemical looping (CL-ODH). In CL-ODH, ethane is oxidatively dehydrogenated to ethylene and water following a typical Mars-van Krevelen mechanism with the participation of lattice oxygen from the catalyst (Catalyst reduction, Reaction 1a) and its exothermic air regeneration (Reaction 1b), further providing heat to the endothermic ethane dehydrogenation to ethylene [22].

CL-ODH (Reduction).

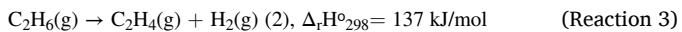
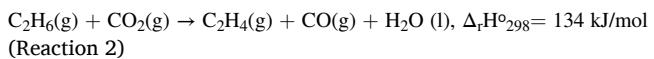


CL-ODH (Regeneration).



Other alternative approaches, currently at the laboratory scale, also using CO₂ as an oxidant to produce value-added ethylene from ethane, are proposed [18,19]. Such processes are attractive because they may lead to a CO₂-negative route in ethylene production. An additional benefit is a significant decrease in energy consumption downstream as hydrogen will not need purification: it will be consumed in situ to convert CO₂ to CO, and the latter could further be used to produce methanol, carbonylate, or hydroformylate other feedstocks. This approach is particularly interesting in view of recent trends to "electrify" steam crackers [23–25].

It is of note that the enthalpies of Reactions 2 and 3 ($\Delta_r H^\circ_{298}$) to produce ethylene from ethane by steam cracking and ODH-CO₂ are very close:



The ODH-CO₂ reaction was first reported by Lunsford et al. [26]

using Li/MgO catalysts. Krylov et al. [27] investigated the ODH-CO₂ using several oxide catalysts (Fe₂O₃, Cr₂O₃, MnO₂) and multi-component systems. In the ODH-CO₂ at 800 °C, MnO₂-based catalysts exhibited high activities but low ethylene selectivity [28]. Nakagawa et al. [29] studied the dehydrogenation of C₂H₆ by CO₂ on several oxides and reported that gallium oxide (Ga₂O₃) is an effective catalyst for this reaction, giving a C₂H₄ yield of 18.6% with a selectivity of 94.5% at 650 °C.

Several reactions may occur in parallel, including oxidative dehydrogenation (ODH), reverse water-gas-shift (RWGS), or dry reforming of ethane (DRE) [30]. For the ODH-CO₂ reaction, precious metals, oxide [31], and carbide [30]-based catalysts are reported. Most of the catalytic systems are based on Pt [32], Ni [33], Co [34], Cr [35,36], Fe [37] oxides deposited on zeolite or oxide carriers.

Only a few Mo-based materials were reported for the ODH-CO₂ of ethane [38–40], but molybdenum carbide is well known as an alternative catalyst to noble metals in the highly selective reduction of CO₂ to CO [41,42]. Very high conversions of ethane in co-processing with CO₂ to produce hydrogen, ethylene, and CO were reported on the catalysts made up of the oxides of cobalt and molybdenum [38,43]. 58% conversion of ethane, 10.3% of CO₂, and 21.9% ethylene yield were achieved over these systems at 700 °C [43]. The conversion of ethane in these studies was higher relative to the thermodynamic equilibrium values of ethane conversion alone due to a significant contribution of secondary reactions [44]. Relatively low selectivity to ethylene showed a significant contribution to the direct ethane dehydrogenation resulting in high hydrogen production [38,43].

Mo₂C supported on SiO₂ was found to be an effective catalyst for the dehydrogenation of ethane to ethylene in the presence of CO₂. The selectivity to ethylene at 600–650 °C was 90–95% at an ethane conversion of 8–30%. At higher temperatures, dry reforming of ethane penalized ethylene yield. It is assumed that Mo oxycarbides formed in the reaction between CO₂ and Mo₂C play an important role in ethane activation [45]. Recently, a Mo-containing catalyst was reported for ODH-CO₂ but again only at 600 °C with relatively modest performance [30,46]. Oxygen from CO₂ appears crucial in cleaving the ethane C-C bond, increasing ethylene production. The addition of a Fe promoter accelerated the formation of surface oxygen species and stabilized them from reduction by ethane, leading to a shorter induction period, higher ethylene yield, and improved stability [30]. However, the main problems with Mo₂C catalysts operating at high temperatures remain the coking, sintering of the active Mo-species from cycle to cycle, and a significant contribution of the dry reforming reaction.

In order to design a stable at high-temperature Mo₂C-supported catalyst, we propose a different approach consisting of the utilization of MoS₂ precursors in place of oxides and embryonic zeolites (EZ) [47] as support in place of silica or alumina. An advantage of embryonic zeolites is the high surface area with a significant micropore volume resulting in the good dispersion and accessibility of all types of active sites [48]. In addition, EZ undergoes changes in surface area after the first heating cycle above 600 °C [48], which stabilizes the metal against sintering while keeping the active sites still accessible for the small molecules. After the first surface reduction, substantially no changes occur with these materials upon consecutive thermal cycles. In this context, the embryonic zeolites as support could also stabilize the formed molybdenum carbide phase at high temperatures. However, the aging of EZ zeolite is a long process, what may lead to the agglomeration of MoO_x-oxides species before carburization. In order to limit the agglomeration of the MoO_x species during the first heating cycle, the idea was to use a MoS₂-precursor supported on EZ. Supported sulfides, especially MoS₂, are also known for CO₂ hydrogenation at high-pressure [49], but using MoS₂ for oxidative or non-oxidative ethane dehydrogenation was never reported to the best of our knowledge.

This work reports the preparation of a novel thermally stable Mo-based catalyst supported on EZ carriers from a MoS₂ – precursor (Mo₂C@EZ), its comprehensive characterization, and catalytic

performances in ODH-CO₂ of ethane.

2. Experimental section

2.1. Preparation of EZ carriers

An all-silica (EZ_{Si}) and an aluminosilicate (EZ_{Al-Si}) embryonic zeolites were used as carriers in all experiments.

The initial gel composition for the EZ_{Si} synthesis was 9 TPAOH:0.25 Al₂O₃:25 SiO₂:430 H₂O:100 EtOH, and for EZ_{Al-Si}, 9 TPAOH:25 SiO₂:430 H₂O:100 EtOH where TPAOH stands for tetrapropylammonium hydroxide [47]. A typical preparation procedure includes mixing the TPAOH solution (20% in water, Alfa Aesar) with distilled water. In the case of synthesis of the embryonic zeolite Al₂(SO₄)₁₈ H₂O (Sigma-Aldrich, 98%) was subsequently added and the system homogenized by stirring. Tetraethyl orthosilicate (TEOS Sigma-Aldrich, 98%) was then added, and the mixture stirred for 6 h leading to the formation of water clear homogeneous sol. The solid product was recovered by freeze-drying (-94 °C under vacuum). The recovered solids were ion-exchanged with 0.5 mol ammonium nitrate solution, washed with distilled water, and dried under air. The resulting samples are referred to as EZ_{Al-Si} and EZ_{Si}. A ZSM-5 (Si/Al=47.6) provided by Tosoh was used as a reference catalyst.

2.2. Metal loading and sulfidation

Mo oxide-decorated catalysts were prepared by incipient wetness impregnation on the embryonic zeolite carriers. The samples were loaded with 5 wt% of Mo and denoted as EZ_{Al-Si}-5%Mo, EZ_{Si}-5%Mo, and ZSM-5-5%Mo. (NH₄)₆Mo₇O₂₄•4 H₂O (Alfa Aesar, 99%) was used as a source of Mo. After drying at room temperature, all samples were calcined at 550 °C for 5 h in static air.

Mo sulfidation was performed under an H₂S/H₂ gas flow (30 mL/min, 10 vol%H₂S). 300 mg of the pelletized sample (35/45 mesh) was loaded in a Pyrex reactor, first heated under an N₂ flow at 140 °C for 2 h, then at 350 °C (2,8 °C·min⁻¹ ramp rate) for 2 h under an H₂S/H₂ flow, cooled down to 180 °C and finally under a flow of dry N₂ to room temperature and kept there for 3 h. The samples were denoted EZ_{Al-Si}-5%MoS₂, EZ_{Si}-5%MoS₂, and the reference ZSM-5-5%MoS₂.

2.3. Physicochemical characterization

The powder X-ray diffraction (PXRD) patterns were recorded on a PANalytical X'Pert Pro diffractometer using the Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The scanning electron micrographs were collected on a MIRA-LMH (Tescan) SEM equipped with a field emission gun.

Nitrogen physisorption was performed on a Micromeritics ASAP 2020 surface area analyzer. The calcined samples were analyzed after degassing at 300 °C. The microporous volume (V_{mic} , cm³·g⁻¹) and the external surface area (S_{ext} , m²·g⁻¹) were obtained from the t-plot method based on the Harkins-Jura equation.

All ²⁷Al NMR measurements were done with 4 mm (o.d.) zirconia rotors spun at 14 kHz on a Bruker Avance 400 spectrometer operating at 100.6 MHz. ²⁹Si MAS NMR was recorded on a Bruker Avance 500 spectrometer operating at 130.3 MHz. TMS was the reference for ²⁹Si, while a 1 M Al(NO₃)₃ solution was used for ²⁷Al. The quantification of the spectra was done by integrating the peaks using the Dmfit program.

The formation of the Molybdenum oxide and sulfide phases was monitored by Raman spectroscopy. The Raman spectra were acquired with a green laser at 532 nm (Jobin Yvon Labram 300 confocal Raman spectrometer coupled to a microscope and CCD detector). Both accumulation time and laser power were adjusted for the samples (embryonic zeolites after metal loading: 40–60 s accumulation 3 times at 50% laser power; after sulfidation: 15–25 s accumulation 3 times at 1% laser power).

Pyridine adsorption monitored by IR spectroscopy was selected to

evaluate the acidity. The spectra were collected on a Nicolet Magna 550 FTIR spectrometer equipped with a DTGS detector at a 4 cm⁻¹ optical resolution with one level of zero filling for the Fourier transform. Prior to measurement, each sample was ground and pressed into a self-supporting disc (diameter: 2 cm, approximately 5 mg·cm⁻²) and activated in a vacuum (ca. 10⁻⁶ hPa) at 450 °C for 2 h at 2 °C·min⁻¹. After cooling to room temperature, a spectrum was recorded as a reference. A pressure of 1.33 hPa of pyridine was established in the cell at room temperature till saturation was reached. The wafer was then heated to 100 °C for 15 min to facilitate pyridine diffusion in the whole disc. Successive evacuations were performed at 100, 150, 200, 250, 300, and 350 °C at 15 min intervals, and spectra were recorded at each step. All spectra were normalized to a 2.5 mg·cm⁻² wafer. The number of acidic sites was determined using the areas of the bands at 1450 cm⁻¹ (Lewis) and 1545 cm⁻¹ (Brønsted). The molar extinction coefficients (ϵ) used for quantification were ϵ_{1545} (B-pyridine) = 1.8 cm·μmol⁻¹, ϵ_{1455} (L-pyridine) = 1.5 cm·μmol⁻¹ [47]. The OMNIC software program was used for data processing.

Thermogravimetric analysis (TGA) was carried out with a SETSYS SETARAM analyser. The temperature was increased from 30° to 800°C at 5 °C/min in reconstituted (80% N₂ + 20% O₂) dry air (40 mL/min).

2.4. Catalytic test

300 mg of the 100–400 μm fraction was used for all the CO₂ oxidative ethane dehydrogenation tests. Before the reaction, all the catalysts were heated at 300 °C under reactants flow for 2 h, as the accuracy of flow rates was verified. The catalysts were brought to the reaction temperature under a flow of reactants at a 10 °C/min ramp rate. After the reaction, the reactor cooled down to room temperature under a dry N₂ flow.

The effluents were analyzed online with a gas chromatograph (Interscience Compact GC) equipped with two thermal conductivity detectors (TCD), and a one flame ionization detector (FID). A Molsieve 5 A, Rt-QBond, Rtx-1 were used to separate light gases (H₂, N₂, CO, CO₂), light hydrocarbons (CH₄, C₂H₄, C₂H₆), and aromatics (from benzene till naphthalene), respectively. In all the experiments, N₂ was used as an internal standard to measure conversion and establish mass balance (Table S1). The mass balance in all the reported experiments was at least 99% (Table S1).

The tests were performed with a C₂H₆/CO₂/N₂ = 49.5/36.5/14 (vol %) mixture in the temperature range 700–800 °C, at atmospheric pressure with a weight hourly space velocity WHSV = 5.9 h⁻¹ (g_{C2H6+CO2}/g_{catalyst} × h).

In order to reveal the catalytic impact of the catalyst on the reaction yield, a blank test without any catalyst was performed under the same operating conditions (same linear velocity, same temperature, same total and partial pressure of the reagents). In the blank test C₂ (ethane), N₂, and CO₂ were co-fed in the same ratio as in the catalytic reaction (C₂H₆/CO₂/N₂ = 49.5/36.5/14 (vol%)). The blank test without a catalyst is referred to in the text as a thermal process ("thermal").

Ethane conversion (C₂ conversion), ethylene selectivity (C₂ = selectivity), and CO selectivity (CO selectivity) were obtained as follows; the sum of the selectivities of the C₃-C₆ fraction and aromatics was labeled heavies:

$$\text{Conversion}(i) = \frac{C_{\text{inlet}}(i) - C_{\text{outlet}}(i)}{C_{\text{inlet}}(i)} \bullet 100\%$$

$$\text{Carbon selectivity } (i) = \frac{F(i)}{\sum F(i)} \bullet 100\%,$$

where F(i)-mol of the C in the product compound.

A techno-economic analysis was done using an Aspen Plus simulator to compare our results with those typical of ethane steam cracking from the literature. The simulations were for a typical industrial-scale

capacity of ethylene production of 1000 kt/year. The physical property databanks and methods as well as ASPEN Plus® models used are summarized in Table S2.

3. Results and discussion

3.1. Characterization of the catalysts

X-ray diffraction (XRD) indicates that on all samples, the embryonic carrier and the supported metal phase are X-ray amorphous (Fig. 1a), and EDX mapping indicates the metal is uniformly distributed on the EZ (Fig. 1b).

The 77-K nitrogen sorption-desorption isotherms of the EZ carriers (Fig. 2a) and the corresponding Mo- and MoS₂ – derivatives (Fig. 2b) show the Type IV isotherms. The mesoporosity is attributed to the intercrystallite spaces between the embryonic units and is observed in all the cases. After impregnation with the metal precursor, micropore volume drops from about 90 cm³/g to 70 cm³/g for the Al-containing embryonic sample (EZ_{Al-Si}) and to 45 cm³/g for all-silica embryos (EZ_{Si}). Mesopore volume decrease is observed only to a very small extent after each treatment for the catalysts. The results show that the metal precursors are mainly located in micropores of the supports.

Raman spectroscopy was used to identify the nature of the metal phase in the EZ-supported catalysts (Fig. 3). The spectrum of EZ_{Si}-5%Mo shows a wide band with two overlapping peaks at 990 cm⁻¹ and 950 cm⁻¹ and two better-resolved bands at 854 cm⁻¹ and 821 cm⁻¹. These bands can be assigned to polymolybdates (950 cm⁻¹, 854 cm⁻¹) [50] and α -MoO₃ (990 cm⁻¹, 821 cm⁻¹) [51] phases. In contrast, the EZ_{Al-Si}-5%Mo spectrum displays only an intense band at 990 cm⁻¹ with a shoulder at 854 cm⁻¹. We assume that both phases are also present on the latter catalyst, the polymolybdate phase being predominant.

The band at 480 cm⁻¹ [52] corresponds to Si-O stretching in the SiO₂ tetrahedra and is attributed to 4-membered rings often reported at 472 cm⁻¹ [53]. Both, EZ_{Si}-IEx and EZ_{Al-Si}-IEx display low-intensity bands around 970 and 1035 cm⁻¹. The 970 cm⁻¹ band is assigned to Si-O stretching vibrations in terminal Si-OH groups [54], while the 1035 cm⁻¹ band is characteristic for the stretching of alkyl chains of the protonated nitrogen atom of the organic template.

The conversion of the oxide to the sulfide phase can also be monitored by Raman spectroscopy. Bands at 370 and 403 cm⁻¹ are attributed to 2 H-MoS₂ phase [55,56]. The wideband with a maximum of about 230 cm⁻¹ is characteristic of silica tetrahedra in a bulk SiO₂ phase and remains unchanged after full oxide conversion.

The high-temperature stability of the catalyst carrier is studied by solid-state ²⁷Al and ²⁹Si NMR. The nature of the silicon environment in the parent all-silica EZ and Mo loaded after one calcination at 550 °C and subsequent calcination at 550 °C and at 700 °C is presented in

Fig. 4a. All spectra display large peaks centered around –110 ppm, and the CP MAS spectrum exhibited a low resolved peak around –100 ppm. Only the parent contains a relatively large amount of Q³ species. Small amounts of Q² species (–97 ppm) can be observed in EZ_{Si}-IEx and EZ_{Si}-5%Mo-550. All spectral deconvolutions are summarized in Table 1. They indicate that metal impregnation increases the number of Q⁴ units along with a full disappearance of the Q³ and Q²'s.

During the high-temperature treatment of silica-alumina embryos (550 °C or consecutive calcination at 550 and 700 °C) after Mo loading, Al is extracted from tetrahedral positions, Fig. 4b while the parent, ion-exchanged with NH₄NO₃, does not contain any octahedral Al. The calcined samples loaded with 5 wt% Mo, three types of aluminum coexist (Al^{IV}, Al^{VI}, and Al₂(MoO₄)₃), witnessing the catalysts alteration at high temperatures.

3.2. Catalytic performances

It is known that above 650 °C, MoO_x and MoS₂ species react with hydrocarbons to produce Mo₂C [57,58]. The mechanism of Mo₂C phase formation from MoS₂ in the presence of CH₄ and H₂ is described [59]. The carbide formation from MoO₃ under C₂H₆ and C₄H₁₀ is also reported [60]. In this contribution, the active Mo₂C phase is obtained in situ by subjecting the Mo-containing precursor in a contact with the mixture of C₂H₆/CO₂ = 1/0.74 at 700 °C. The hypothesis on Mo₂C formation is based on the typical profile of the TG curve [61] and on the observation of the characteristic bands for the graphitized carbon in Raman spectra synthesized with non-methane carburization agent [62,63]. The TGA curves of the spent Mo₂C-containing samples demonstrated a slight weight increase up to 470 °C due to the oxidation reaction of Mo₂C to MoO₃ (Fig.S3). However, the analysis of Mo₂C on the spent catalysts by Raman spectroscopy is a difficult task. The sulfidic form on the precursor is confirmed by the two bands around 370 and 403 cm⁻¹ (Fig. 5), both bands are dispersed on the spent Mo₂C-containing samples. That shows the transformation of the MoS₂-species to a different species. In addition, two new intense bands are detected in the region of C-C vibrations – (band D) at 1350 and (band G) 1600 cm⁻¹ on the sample after the reaction. They are typically attributed to the graphitized carbon (Fig. 5) [64]. The intensity ratio of G (1580 cm⁻¹) to D (1350 cm⁻¹) band reflects the graphitization degree of catalysts [63]. These data suggest that the excess of methane led to the formation of graphitic carbon with the characteristic bands at 1350 and at 1600 cm⁻¹, which are also typically observed when the Mo₂C phase is formed [63]. The same covering of Mo-C bands was demonstrated under ethane, while XRD confirmed the formation of the claimed phase [63].

3.2.1. Impact of Mo-precursor:MoO_x vs MoS₂

Thermal, i.e., the non-catalytic transformation of the mixture of

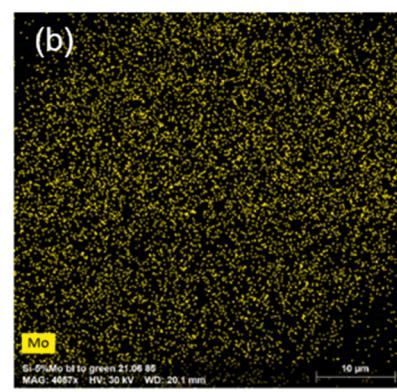
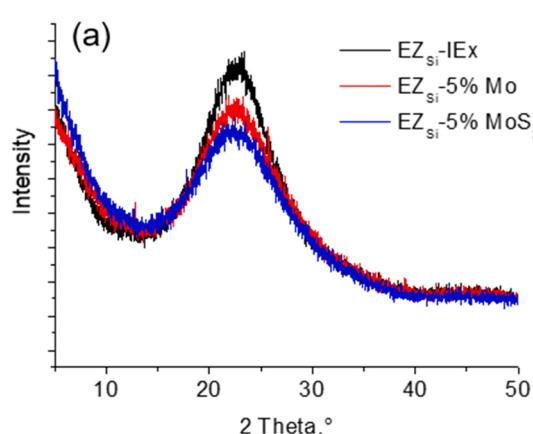


Fig. 1. a) XRD patterns of EZ_{Si}-IEx, EZ_{Si}-5%Mo, EZ_{Si}-5%MoS₂; b) EDX elemental mapping of Mo in EZ_{Si}-5%Mo.

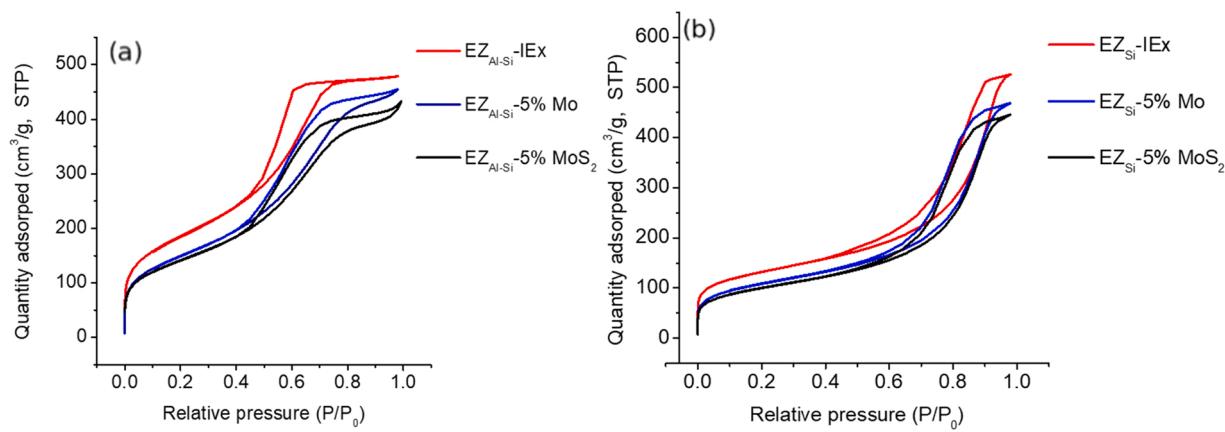


Fig. 2. N_2 adsorption-desorption isotherms: a) $\text{EZ}_{\text{Al-Si}}$ -based; b) EZ_{Si} -based.

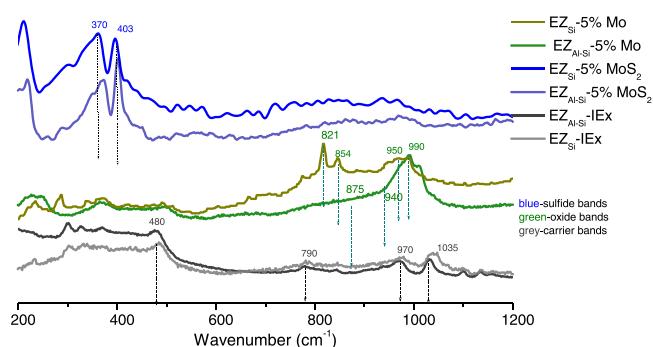


Fig. 3. Raman spectrum of EZ decorated with molybdenum oxide and sulfide phases.

ethane and CO_2 at 700°C , results in ethane to ethylene conversion level, which is close to the thermodynamic equilibrium, with the ethylene selectivity above 95%. However, only a very limited CO_2 conversion is observed in this case. In contrast, the presence of the Mo_2C -supported on embryonic zeolite catalyst, formed from MoS_2 or MoO_x -precursors ($\text{EZ}_{\text{Si}}\text{-}5\%(\text{Mo}_2\text{C})_S$ or $\text{EZ}_{\text{Si}}\text{-}5\%(\text{Mo}_2\text{C})_O$), leads to a significantly higher CO_2 conversion. One can also see that the $\text{EZ}_{\text{Si}}\text{-}5\%(\text{Mo}_2\text{C})_S$ from MoS_2 -precursor performs CO_2 transformation substantially without decreasing the ethane conversion in comparison with the one in the thermal process (Fig. 6a). Moreover, the selectivity to ethylene is higher (Fig. 6b). In contrast, the MoO_x -derived catalyst displays not only lower CO_2

conversion in comparison with the MoS_2 -derived catalyst but also significant activity in ethylene hydrogenation back to ethane and very high methane selectivity (Fig. 6a, b).

The results summarized in Table S3 show that only a few by-products are produced in all the cases. The MoS_2 -derived catalyst also demonstrates higher stability than the MoO_x -derived one (Fig. S1) and the highest selectivities in all cases. Therefore, the MoS_2 -derived catalyst was selected for further investigation.

3.2.2. Impact of the catalyst carrier

The performances in the ODH- CO_2 reaction of a series of MoS_2 -derived catalysts supported on EZ of different acidity ($\text{EZ}_{\text{Si}}\text{-}5\%(\text{Mo}_2\text{C})_S$, $\text{EZ}_{\text{Al-Si}}\text{-}5\%(\text{Mo}_2\text{C})_S$, ZSM-5-5% $(\text{Mo}_2\text{C})_S$) was evaluated. An embryonic zeolite and a conventional ZSM-5 with a crystal size of about $1\ \mu\text{m}$ with a similar Si/Al atomic ratio were used for the study. The Bronsted acidity (BAS) and the Lewis acidity (LAS) of the supports before metal impregnation was assessed by FTIR adsorption of pyridine (Table 2). While the siliceous EZ_{Si} did not display any acidity, the Al-containing embryonic zeolite ($\text{EZ}_{\text{Al-Si}}$) showed some acid properties (Table 2). As

Table 1

Relative percentage of Q^2 , Q^3 , and Q^4 silicon environments in EZ_{Si} -parents and calcined derivatives.

Sample	Q^2	Q^3	Q^4
$\text{EZ}_{\text{Si}}\text{-IEx}$	7	48	45
$\text{EZ}_{\text{Si}}\text{-5\%Mo-550}$	2	22	76
$\text{EZ}_{\text{Si}}\text{-5\%Mo-550-700}$	–	27	73

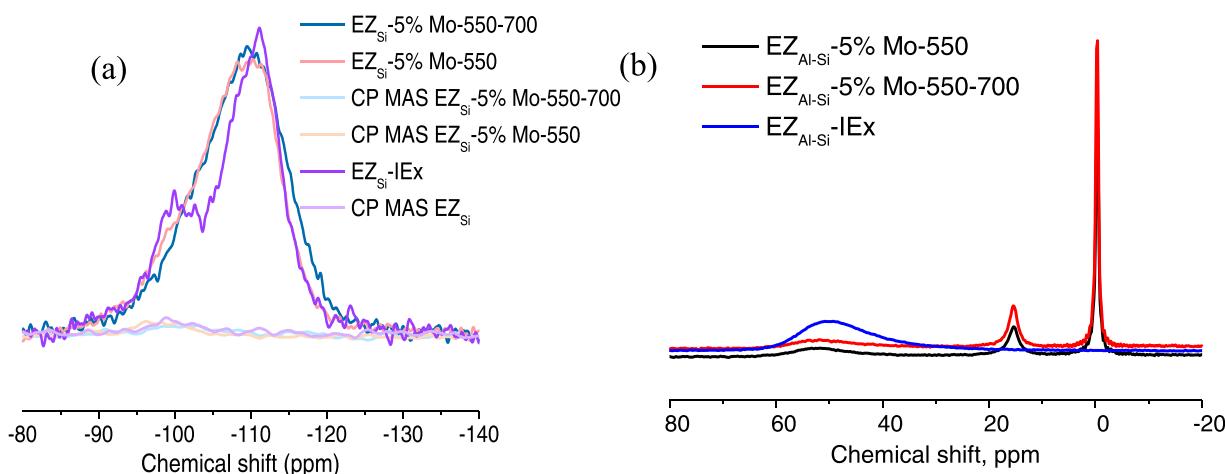


Fig. 4. Solid-state NMR analysis of the parent materials after ion exchange and Mo-loading: a) ^{29}Si NMR (1pulse) and CP MAS spectra; b) ^{27}Al NMR spectra.

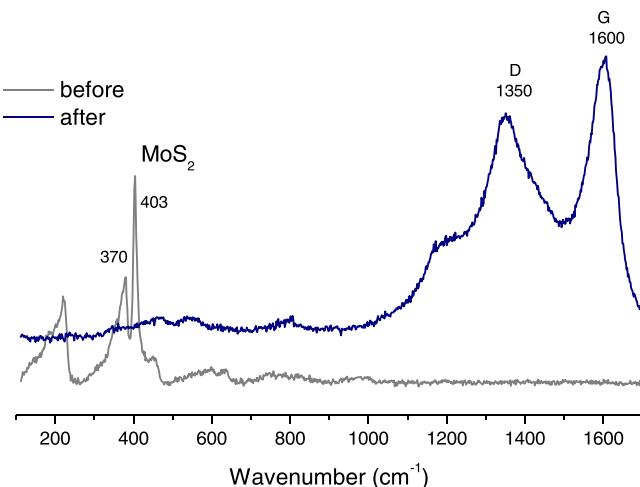


Fig. 5. Raman spectrum of embryonic zeolite decorated with sulfide phase before and after the catalytic test at 700 °C over EZ_{Si}-5%Mo₂C_S.

expected, the highest acidity was measured on the zeolite carrier (ZSM-5).

The initial CO₂ and C₂H₆ conversions on the catalysts prepared on acidic support (ZSM-5-5%Mo₂C_S and EZ_{Al-Si}-5%Mo₂C_S) were significantly higher than on siliceous one (Fig. S2). In the case of ZSM-5-5%Mo₂C_S, ethane and CO₂ conversions were 37% and 30%, respectively. However, the main products were coke and aromatics, leading to rapid deactivation: down to 18% C₂H₆ and 13% CO₂ after 140 min-on-stream, respectively. The result showed that the strong acidity of the support, which is typical for the zeolites is not desirable and leads to many side reactions.

The embryonic zeolite with a bulk Si/Al ratio close to the ZSM-5 one showed lower acid site concentration and, as a consequence, slower deactivation in comparison to the one on ZSM-5 support. It should be mentioned that the selectivity patterns on the Al-containing EZ_{Al-Si}-5%Mo₂C_S catalyst and on Al-free EZ_{Si}-5%Mo₂C_S catalysts looked more similar. One of the potential advantages of the Al-containing embryonic zeolite is the higher activity in CO₂ hydrogenation. However, higher coke content, in addition to higher methane selectivity, makes the acidity a disadvantage in this reaction (Fig. S3).

3.2.3. Performance of Al-free EZ_{Si}-5%Mo₂C_S in ODH-CO₂ of ethane

The selected purely siliceous EZ_{Si} material showed to be advantageous in the dispersion and stabilization of Mo₂C while preventing deactivation due to coke formation (Fig. 7a, Fig. S3). Indeed, MoS₂-precursor supported on EZ extends the operating temperature range of

Mo₂C catalysts compared to previously published results [36,37,45], in addition to suppressing the unwanted side reactions of methanation and dry-reforming. Remarkably, the selectivity to ethylene is even higher at the same process temperature than in the thermal process (Fig. 7b).

The difference in ethane's catalytic and thermal conversion is due to some ethylene hydrogenation. Although the activity in ethylene hydrogenation is significantly lower on the catalyst than the one in CO₂ conversion to CO, it is worth comparing the selectivity at different temperatures at the same level of conversion.

The selected catalyst (EZ_{Si}-5%Mo₂C_S) was tested at different temperatures, and its performance was compared with the thermal (without catalyst) transformation of ethane in the presence of CO₂ (Fig. 8). Due to some partial hydrogenation, the apparent ethane conversion level at the same temperature was slightly lower than in the thermal process (Fig. S4). In order to compare the results, the data were linearly extrapolated to the same level of conversion. Three conversion levels of ethane were selected for the comparison: low conversion (15%), mid conversion (40%), and high conversion (66%). In contrast to literature data on Mo₂C type of materials [45], one can see that at about 50% of CO₂ conversion to CO (reverse water-gas-shift reaction), the methanation and the dry reforming remained insignificant in the studied system (Fig. 8). In all cases, the ethylene selectivities in -CO₂ of ethane were found very close between catalytic and non-catalytic processes. The impact on ethylene selectivity did not exceed 1–3% for all the conversion levels of ethane, which could be considered insignificant. One can see that the presence of catalyst allows achieving a 50% conversion level of CO₂ without decreasing the selectivity to ethylene in comparison with the thermal process at the conversion of ethane up to 66% (Fig. 8). All the results were obtained in the temperature range 700–800 °C what is the industrially relevant temperature range for the ethane cracking. A detailed comparison with the ethane cracking of the obtained catalyst performance is given below.

3.3. Techno-economical analysis of the ODH-CO₂ process based on an EZ_{Si}-5%Mo₂C_S catalyst

As mentioned in the introduction section, the emerging technological solutions aim to produce ethylene from ethane with lower CO₂

Table 2

Acid site concentration on ZSM-5 and Al-containing embryonic zeolite measured by FTIR with pyridine probe molecule.

Sample	LAS, $\mu\text{mol/g}$	BAS, $\mu\text{mol/g}$
ZSM-5 (Si/Al=47)	235	1094
EZ _{Al-Si} (Si/Al=43)	57	185

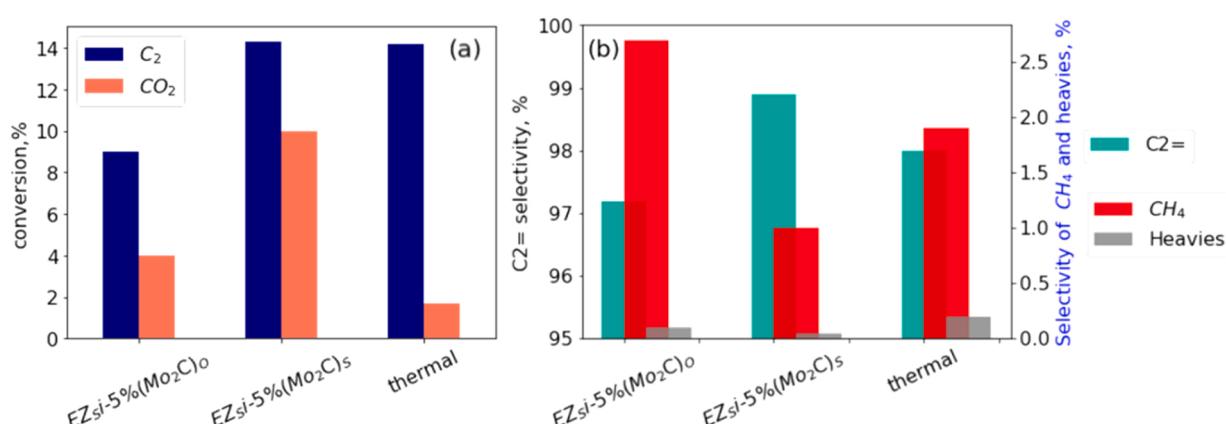


Fig. 6. ODH-CO₂ of ethane on EZ_{Si}-5%Mo₂C_O, EZ_{Si}-5%Mo₂C_S, and without catalyst: a) conversion of CO₂ and ethane; b) selectivities to the products (coke-free basis, 700 °C, C₂H₆/CO₂ = 1/0.74, WHSV = 5.9 h⁻¹, average level for 2–5 hour-on-stream).

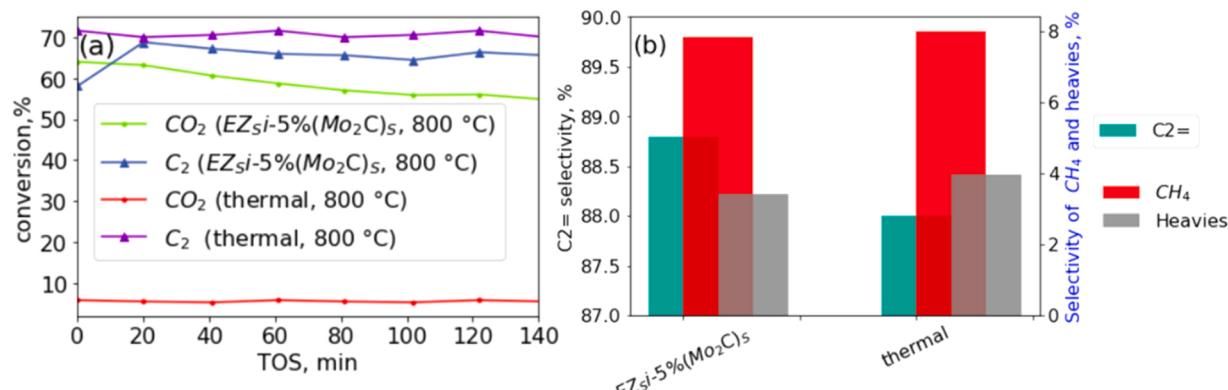


Fig. 7. ODH-CO₂ of ethane (C₂) on EZ_{Si}-5%Mo₂C_S and without catalyst: a) conversion of CO₂ and ethane as a function on time-on-stream; b) selectivities to the products (coke-free basis, T = 800 °C, P = 1 atm, C₂H₆/CO₂ = 1/0.74, WHSV = 5.9 h⁻¹).

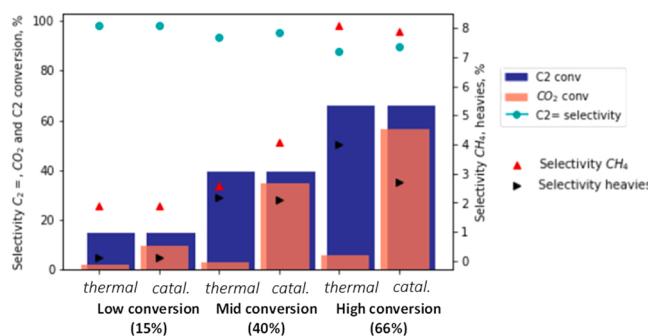


Fig. 8. Comparison of catalytic (EZ_{Si}-5%Mo₂C_S) and thermal performances in ODH-CO₂ of ethane at the same conversion level of ethane (coke-free basis, C₂H₆/CO₂ = 1/0.74, WHSV = 5.9 h⁻¹).

emissions in comparison with an ethane cracker.

The endothermic cracking of ethane (its C-C and C-H bonds require dissociation energies of 345 and 413 kJ/mol, respectively) to ethylene yield is limited. It requires high temperature and leads to the formation of side products such as aromatics and light gaseous. The catalytic conversion of ethane to ethylene in the presence of an oxidant is a potential solution to the problems outlined above. The ODH-E technology recently developed by Linde/Clariant reports CO₂ emissions reductions in the 23–32% range compared to conventional steam cracking [18]. The EcoCatalytic's CL-ODH technology also claims a 64% substantial reduction in CO₂ emissions compared to a state-of-the-art ethane steam cracker of the same capacity [22]. In the case of the state-of-the-art ethane steam cracker, hydrogen is the by-product. Such hydrogen could alternatively be used as a fuel for heat generation, leading to overall CO₂ emission reduction.

In such a broader context, oxidative dehydrogenation of ethane in the presence of CO₂ (ODH-CO₂) is a promising economical and environmental alternative. This process directly utilizes hydrogen to transform CO₂ into CO, which could further be used as the precursor for producing valuable chemicals, mitigating CO₂ emissions while simultaneously achieving ethane dehydrogenation. This process can not only reduce CO₂ emission but also simplifies production slate processing by reducing CH₄ and heavies production.

Steam cracking proceeds through free-radical mechanisms [65], which are inherently characterized by a vast number of species and reactions leading to wide product distribution. Moreover, in steam crackers, acetylene is a by-product. Typically, the acceptable acetylene contaminant level in polymer grade ethylene products is 1 ppmv or lower. Since acetylene will fractionate with ethylene, it needs to be removed before the C₂ fractionation step. An acetylene hydrogenation

unit is often required to convert it to ethylene. Consequently, the downstream processing of a steam cracker requires multiple separation units, as shown in Fig. S5a.

In a state-of-the-art ethane steam cracker, the traces of CO are hydrogenated to CH₄, and the unconverted H₂ is of low grade with a significant amount of methane. The ODH-CO₂ process results in a significant amount of CO, significantly lower methane production, and some remaining hydrogen. So, the light end from an ODH-CO₂ could be considered as syngas, which after an adjustment of hydrogen content, could be directly suitable for MeOH synthesis.

ODH-CO₂ results in a lower amount of heavies, with almost no C₃ fraction and no acetylene, detected in the effluent of the reactor, as seen in Table 3. That is very interesting for separation and, eventually, for the energy balance. On the other hand, the C₂/CO₂ fraction should not be necessarily separated and could be recycled back to the reaction session as a feedstock (Fig S5b).

Fig. 9 highlights the unit operations of a conventional SC plant and an ODH-CO₂ plant. The ODH-CO₂ requires 50% less unit operations compared to an ethane cracker. One can see that ODH-CO₂ may bring significant advantages in terms of investment costs and separation duties and therefore reduce CAPEX and OPEX.

Regarding energy consumption, ethylene production via steam cracking of ethane is very energy consuming: producing 1 ton of ethylene typically requires 21 GJ of thermal energy (process energy consumed in pyrolysis and separation) and results in approximately 1.2 tons of CO₂ emissions [5]. In our case, the simulation of the ODH-CO₂ process indicates an energy consumption of 17.4 GJ of thermal energy to produce 1 ton of ethylene and consumes 1,09 tons of CO₂.

Table 3
Comparison of steam cracking (SC) of ethane and ODH-CO₂.

	SC of ethane [66], 845 °C-outlet	ODH-CO ₂ [this work]
Ethane Conversion (%)	65.0	66.1
Carbon Yield (dry mol%)		
CO	0.00	27.34
CO ₂	0.00	20.71
CH ₄	3.40	4.81
C ₂ H ₂	0.50	0.00
C ₂ H ₄	56.10	27.29
C ₂ H ₆	35.00	19.46
C ₃ H ₆	1.20	0.00
C ₃ H ₈	0.10	0.00
C ₄ H ₆	2.10	0.00
C ₄ H ₈	0.20	0.00
C ₄ H ₁₀	0.20	0.30
C ₅ 's	0.60	0.10
Aromatics (benzene, toluene)	0.60	0.08

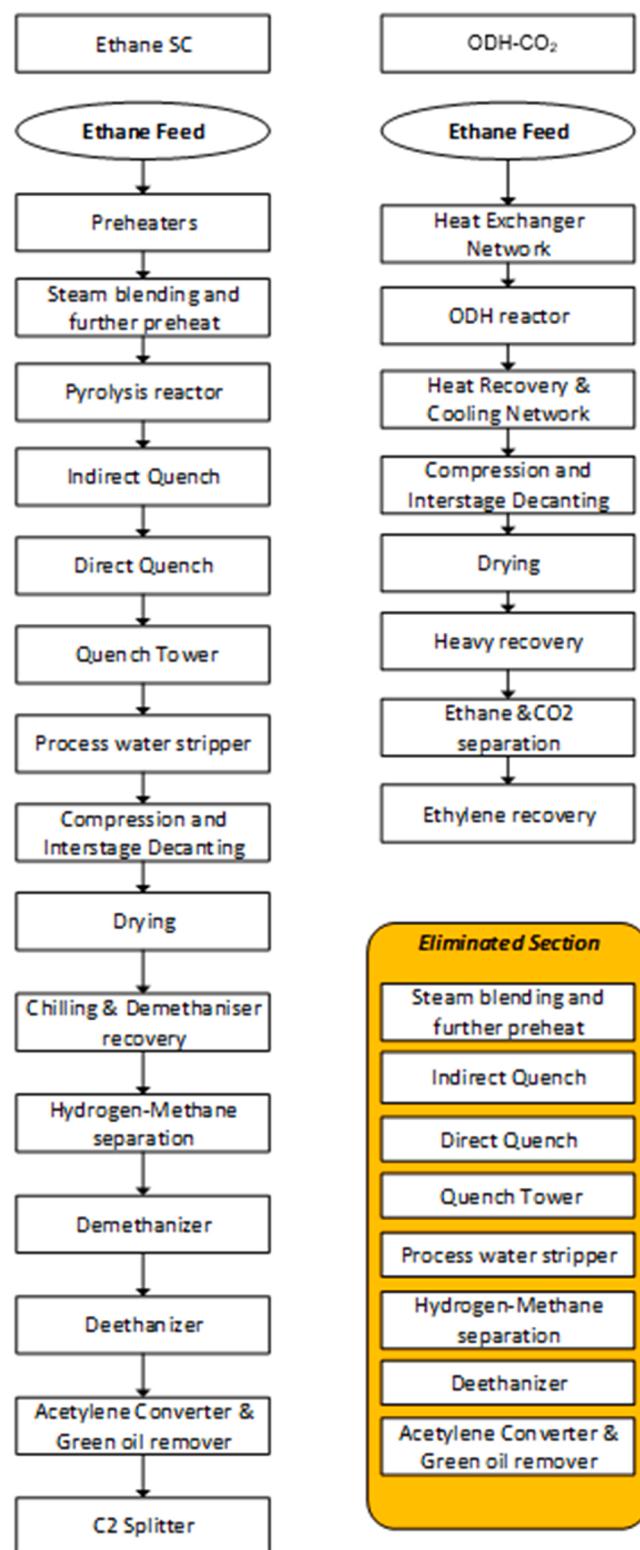


Fig. 9. Comparison in term of unit operations between SC and ODH-CO₂ ([55]).

Therefore, if ODH-CO₂ is implemented based on the current catalytic results, the reduction of CO₂ would be up 109% in comparison with the state-of-the-art ethane cracker making the technology CO₂ negative.

4. Conclusions

Embryonic zeolites show potential as supports for Mo₂C active species in ODH-CO₂. Supported metal sulfides proved to be efficient precursors of the Mo₂C active phase, which allows the designing of novel thermally stable and highly active catalysts for CO₂ hydrogenation in co-processing with alkenes. This “sulfide” route shows a clear advantage over the “oxide” one and requires only about 5 wt% of Mo.

Although a detailed formation mechanism from MoS₂ to Mo₂C is still under investigation, it seems that MoS₂ supported on embryonic zeolites prevents sintering of the Mo-species during the carbide formation and results in a more active and stable catalyst for ODH-CO₂ of ethane. The latter allows operating at higher temperatures, avoiding dry reforming and methanation side reactions while producing more selectively ethylene.

The supported Mo₂C displays a good activity in CO₂ hydrogenation without negatively impacting the thermal C₂ conversion to ethylene at a conversion up to 66%. The resulting ODH-CO₂ process could lead to a potentially promising CO₂-negative technology with a much-reduced separation section due to a lower amount of heavies, no acetylene production, and better carbon efficiency. ODH-CO₂ thus brings significant advantages in terms of investment (CAPEX) and operating (OPEX) costs of a greener process.

CRediT authorship contribution statement

Vera Bikbaeva: Investigation, Methodology, Writing – original draft. Nikolay Nesterenko: Conceptualization, Supervision, Writing – review & editing. Thanh-Son Nguyen: Investigation. Stanislav Konnov: Investigation. Valentin Valtchev: Conceptualization, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Vera Bikbaeva, Stanislav Konnov, Jean-Pierre Gilson, Valentin Valtcheva reports financial support was provided by National College of Engineers of Caen. Nikolay Nesterenko, reports financial support was provided by TotalEnergies SE. Thanh-Son Nguyen reports financial support was provided by TotalEnergies SE. Nikolay Nesterenko reports a relationship with National College of Engineers of Caen that includes: funding grants. no conflict of interest to declare.

Data availability

No data was used for the research described in the article.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2022.122011.

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